D E C L A R A T I O N

In the matter of U.S. Patent
Appln. Ser. No. 09/374,344
in the name of TOTO LTD.

I, KONNO Akio , of Kyowa Patent and Law Office, 2-3, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare and say:

that I am thoroughly conversant with both the Japanese and English languages; and,

that the attached document represents a true English translation of Japanese Patent Application No. 7-205019 filed on July 8, 1995.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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KONNO Akio

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Title of the Invention: OUTDOOR MEMBER AND METHOD FOR FORMING THE SAME

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Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome, Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto CHIKUNI

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome, Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Atsushi KITAMURA

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome, Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Toshiya WATANABE

Inventor:

Address: c/o Toto Ltd., 1-1, Nakashima 2-Chome, Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: Makoto HAYAKAWA

Applicant:

Identification Number: 000010087

Postal code: 802
Address: 1-1, Nakashima 2-Chome, Kokura-Kita-Ku, Kitakyushu-Shi, Fukuoka-Ken

Name: TOTO LTD.
Representative: Shigeru Ezoe

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(Translation) 7-205019

SPECIFICATION

1. TITLE OF THE INVENTION

Outdoor member and method for forming the same

[Claims]

1. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.

2. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a modified silicone resin thereon.

3. An outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized.

4. An outdoor member of either one of claim 1, claim 2, and claim 3, wherein the surface layer further includes silver.

5. An outdoor member of either one of claims 1 through 4, wherein the outdoor member is a member for external walls.

6. A method for forming the member claimed in either one of claims 3 through 5, wherein a light containing ultraviolet light is irradiated to the surface of the substrate after forming the surface layer made of a photocatalyst and a silicone resin.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an outdoor member difficult to be contaminated with city-type contaminants such as combustion products, which member includes: the one for external walls of sky-scraping buildings and general structures and buildings; the one for casings of automobiles, electric cars, trains, airplanes, and ships; the one for legs of overhead bridges, footbridges, and bridges; the one for outdoor members such as signboards, fences, markings, stacks, lighthouses, guard rails, big wheels, outdoor statues, outdoor sculptures, outdoor monuments, memorials, and oil tanks. The present invention also relates to a method for forming the outdoor member.

[0002]

[Description of the Prior Art]

Black striped contamination appeared on external walls of structures and buildings comprises hydrophobic materials such as carbon black which is a combustion product (according to "Lecture bulletin of Annual Meeting of Architectural Institute of Japan, 1987). The carbon black attaches to the surface of structures and buildings, and is carried by water flowing down on the surface to adhere to the structure surface (according to Report on Structure System, Architectural Institute of Japan, No. 404, 1989, 10)

Accordingly, a material having a hydrophobic surface is likely contaminated, and a material having a hydrophilic surface is difficult to be contaminated because hydrophobic materials such as combustion product carbon black are washed

off.

Based on the findings, application of a hydrophilic coating onto the surface of external walls of structures and buildings has become a recent preventive measures to avoid contamination in a shape of black vertical stripes on the external wall surface thereof ("Polymer" vol.44, 1995).

[0003]

On the other hand, a method for cleaning sold contamination is disclosed in Japanese Patent Laid-Open No. 51646/1995. According to the disclosure, a photo-semiconductor is supported on a surface of solid which is expected to be contaminated by attaching organic matter in air, then a light containing ultraviolet light is irradiated to the photo-semiconductor to decompose the organic matter attached to the surface of the solid.

[0004]

[Problems to be Solved by the Invention]

The method solely applying a hydrophilic coating onto external walls, however, failed to sustain the hydrophilicity for a long term. The presumable reason of failing to sustain the hydrophilicity is that materials such as lower carboxylic acid and surface active agent which have functional groups of both hydrophilic and hydrophobic properties attach to the wall surface with time, thus the coating is gradually hydrophobicized.

[0005]

As for the method of cleaning solid contamination by supporting a photo-semiconductor on the surface of solid which is expected to be contaminated by attaching organic matter in air, then by irradiating a light containing

ultraviolet light to the photo-semiconductor to decompose the organic matter attached to the surface of the solid, the decomposition of organic matter has to be performed solely by the action of photo-semiconductor, which means that the intensity of ultraviolet light needs as high as 7 mW/cm^2. Therefore, it is impossible to clean the solid contamination solely by solar rays.

[0006]

In this respect, an object of the present invention is to provide an outdoor member that is able to prevent the occurrence of vertical black stripes on external walls of structures and buildings for a long period.

[0007]

[Means to Solve the Problems]

To solve the above-described problem, the present invention provides an outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.

[0008]

The present invention provides an outdoor member comprising a substrate, and a surface layer made of a photocatalyst and a modified silicone resin thereon.

[0009]

According to a preferred mode of the present invention, a substrate is provided with a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized.

[0010]

According to a preferred mode of the present invention, the surface layer further includes silver.

[0011]

The present invention provides a method for forming a member comprising a substrate being provided with a surface layer made of a photocatalyst and a resin in which a modified portion of a modified silicone resin is polarized, wherein a light containing ultraviolet light is irradiated to the surface of the substrate after forming the surface layer made of a photocatalyst and a silicone resin.

[0012]

[Best Mode of the Invention]

The term "outdoor member" means a member or a part of the member which is used in outdoor exposed to sun rays, which member includes: the one for external walls of sky-scraping buildings and general structures and buildings; the one for casings of automobiles, electric cars, trains, airplanes, and ships; the one for legs of overhead bridges, footbridges, and bridges; the one for outdoor members such as a signboards, fences, markings, stacks, lighthouses, guard rails, big wheels, outdoor statues, outdoor sculptures, outdoor monuments, memorials, and oil tanks.

[0013]

For an outdoor member, by forming a surface layer made of a photocatalyst and a hydrophilic material on the substrate, the effect of preventing contamination of black vertical stripes is sustained owing to the hydrophilic material for a long time. The effect is functioned by the photocatalyst and solar rays, which action is described below.

Even when materials such as lower carboxylic acid and surface active agent which have functional groups of both

hydrophilic and hydrophobic properties onto the surface of substrate, the hydrophobic functional groups are oxidized or decomposed by ultraviolet light contained in solar rays and by photocatalyst, so the hydrophilicity is sustained. As a result, outdoor members reject the adhesion of black vertical stripe contamination comprising hydrophobic materials such as combustion product carbon black for a long time.

[0014]

The term "hydrophilic material" means a material which is compatible rather with water than with oil. In concrete terms, the material has a greater contact angle with water than that with oil such as oleic acid. That type of material is the one having a strong contribution of hydrogen bond energy and dipole energy to surface energy. Examples of that type of material are inorganic oxides, resin having lots of N-H bond, S-H bond, and O-H bond on the surface thereof.

[0015]

The term "photocatalyst" means a material which forms electron-positive hole pair under irradiation of light having energy of forbidden band width or more, and which enhances reaction directly or indirectly owing to the formed electron or positive hole. Examples of the photocatalyst are titanium oxide (anatase type, rutile type), zinc oxide, tin oxide, iron oxide, tungsten oxide, strontium oxide, di-bismuth trioxide.

[0016]

For an outdoor member, by forming a surface layer made of a photocatalyst and a modified silicone resin on the

substrate, the hydrophobic functional groups of alkyl and the like in modified silicone resin are oxidized or decomposed by irradiation of solar rays, thus forming a hydrophilic surface. Once formed hydrophilic surface sustains its hydrophilicity even when materials such as lower carboxylic acid and surface active agent which have functional groups having both hydrophilic and hydrophobic properties adsorb because photocatalyst and ultraviolet light contained in solar rays successively oxidize or decompose the hydrophobic functional groups. As a result, outdoor members reject the adhesion of black vertical stripe contamination comprising hydrophobic materials such as combustion product carbon black for a long time.

Many of modified silicone resins have excellent flexibility. These flexible resins include siloxane resin, silicone rubber, cross-linked silicone resin. With these modified silicone resins, bending is possible after forming the surface layer made of a photocatalyst and a modified silicone resin on the substrate surface. The effect cannot be expected for a silicone resin to which a surface layer made of silicone resin and photocatalyst from the beginning. [0017]

An outdoor member, of which substrate is covered with a surface layer made of a photocatalyst and a hydrophilic material, is easily prepared by, for example, forming the surface layer made of a photocatalyst and a modified silicone resin, then polar-processing the modified section of the modified silicone resin.

The term "polar-processing" means a process to give polarity by applying hydrogen bond and the like to the

modified section of the modified silicone resin comprising hydrophobic groups. An example of that type of processing is the one to oxidize or decompose the modified section of a modified silicone resin. Irradiation of light containing ultraviolet, ozone processing, and plasma processing are preferable examples of the polar-processing.

Among these processing methods, irradiation of light containing ultraviolet light is most simple one because the presence of photocatalyst in the surface layer makes polar-processing readily performed within relatively short time even under relatively weak irradiation of ultraviolet light. Applicable light containing ultraviolet light includes solar rays, light of BLB lamp, fluorescent lamp, mercury lamp, xenon lamp, and halogen lamp.

[0018]

It is preferable to add an anti-bacterial metal such as silver, copper, and zinc to the surface layer because the preventive effect against algae, mildew, moss formation.

In particular, addition of silver is preferable because the preventive effect against algae, mildew, moss formation is expected while remaining the performance of photocatalyst to sustain hydrophilicity and remaining the recovery effect.

[0019]

[Embodiments]

The present invention is described in more detail in the following referring to experimental examples.

(Example 1)

A solution of siloxane resin containing a curing agent was applied onto an aluminum substrate (10 cm square). The substrate was treated by heat at 150℃ to prepare an

intermediate member P. A liquid was prepared by: adding a siloxane resin to a nitric acid deflocculating titanium oxide sol having an average particle size of 0.01 μm to a concentration of 50 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting the mixture by propanol; and adding a curing agent to the mixture. Thus prepared liquid was applied onto the surface of the intermediate member P. Then the member P was treated at 150℃ to obtain a specimen A. A BLB lamp light (0.5 mW/cm^2) was irradiated against the specimen A for 10 hours to obtain a specimen B. Separately, a liquid was prepared by: adding a siloxane resin to a mixture of a nitric acid deflocculating titanium oxide sol having an average particle size of 0.01 μm and an aqueous solution of silver nitrate to a concentration of 50 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting the mixture by propanol; and adding a curing agent to the mixture. Thus prepared liquid was applied onto the surface of a separate intermediate member P. Then the member P was treated at 150℃, to which a BLB lamp light (0.5 mW/cm^2) was irradiated for 10 hours to obtain a specimen C. The specimens A through C, the aluminum substrate, and the intermediate member P were mounted to the specimen-holding section of a device shown in a Fig. 1. The device was allowed to stand on the rooftop of a five-storied building. Then, the change of attaching state of black vertical stripe contamination and the change of hydrophilicity were observed with time. The hydrophilicity was determined by the contact angle with water.

[0020]

The change of attaching state of black vertical stripe contamination with time was evaluated by visual observation and by the color difference at various positions in the same specimen.

Visual observation found vertical stripe contamination on the aluminum substrate and the intermediate member P after 1 week, though there was no vertical stripe contamination on the specimens A through C. On the specimen A, there was observed an irregular pattern contamination after a rain in the first day. With elapsed time, however, the surface of the specimen A was hydrophilicized by the solar ray irradiation, and succeeding rains washed off the irregular pattern contamination to give clean surface similar with that of the specimens B and C.

After 1 week has passed, the aluminum substrate and the intermediate member P showed significant contamination on their whole surface area, resulting in the increase of color difference to a range of from 1 to 4. To the contrary, the specimens A through C showed very little change in color difference after 1 week compared with original state.

For the aluminum substrate and the intermediate member P after 1 week, vertical stripe contamination was observed. Depending on the position of observation, there observed a color difference of 3 on the aluminum substrate and 1.2 on the intermediate member P. For the specimens A through C, however, no vertical stripe contamination appeared, and their color difference was within 0.1 even when the observation positions were changed.

As for the degree of hydrophilicity, the aluminum

substrate and the intermediate member P gave original value of around 60 deg. and 90 deg., 1 week respectively, and become to around 70 deg. abter for both of them, or became to hydrophobic property. For the specimens B and C, however, around 3 deg. of original hydrophilicity became less than 1 deg. after 1 week. The specimen A sowed around 90 deg. of original hydrophilicity, and became less than 1 deg. after 1 week.

These findings proved that an outdoor member (the specimens B and C) having a substrate and a surface layer made of a photocatalyst and a resin in which the modified section of modified silicone resin was polarized thereon does not form vertical stripe contamination because the hydrophilic surface is sustained, and that an outdoor member (the specimen A) having a substrate and a surface layer made of a photocatalyst and a modified silicone resin thereon does not form vertical stripe contamination because the surface is hydrophilicized by solar rays and because the hydrophilic surface is sustained.

[0021]

The specimen B was coated with oleic acid, and was immersed to water in a position that the surface of the member becomes horizontal. The contact angle with oleic acid was immediately increased to form droplets, which droplets were then floated. For the aluminum substrate and the intermediate member P, however, dipping them horizontally facing the surface horizontal sustained the wetted state of oleic acid. That is, when the hydrophilic surface is sustained and when the member is left outdoor, rain and the like enters between the member surface and the

hydrophobic black vertical stripe contamination, thus making the black vertical stripe contamination difficult to adhere.
[0022]

The specimen B, the aluminum substrate, and the intermediate member P were wetted with water, and were set to the device shown in Fig. 1, which device was then allowed to stand. After 30 min, the specimen B was dried, and the aluminum substrate and the intermediate member P left water droplets thereon. The phenomenon should come from the result that the specimen B was uniformly wetted with water, thus the thick water film portion should be difficult to appear. Consequently, it was confirmed that, when the present invention is applied to an outdoor member, there is an additional advantage of quick drying of member. That kind of advantage is preferable in car-wash for prompt drying, or particularly preferable for a member of vehicle casing.
[0023]

Effect of maintaining performance of hydrophilicity and recovery of hydrophilicity was determined on the specimen B. The effect of maintaining performance of hydrophilicity was evaluated from the contact angle with water before and after the irradiation of BLB lamp light ($0.5\ mW/cm^2$) for 1 month. Effect of recovery of hydrophilicity was determined by the change of contact angle with water with time by wiping the surface of the specimen with alcohol to increase the contact angle of the surface with water, then irradiating BLB lamp light ($0.5\ mW/cm^2$)

Both immediately after the irradiation and after 1 month from irradiation, the contact angle with water

remained below 1 deg., at a favorable angle, to prove the sustained effect of the hydrophilicity.

After wiping off the surface with alcohol to increase the contact angle of the surface with water, BLB lamp light (0.5 mW/cm^2) was irradiated to the surface to observe the change of contact angle with water with time. About 1 hour or irradiation recovered the contact angle with water from 30 deg. to about 1 deg.

[0024]

(Example 2)

A solution of siloxane resin containing a curing agent was applied onto an aluminum substrate (10 cm square). The substrate was treated by heat at 150℃ to prepare an intermediate member P.

A liquid was prepared by: adding a siloxane resin to a nitric acid deflocculating titanium oxide sol having an average particle size of 0.01 μm to a concentration of, separately, 5 wt.%, 10 wt.%, 50 wt.%, 80 wt.%, and 95 wt.% to the weight sum of the solid titanium oxide and the siloxane resin; diluting each mixture by propanol; and adding a curing agent to each mixture. Thus prepared each liquid was applied onto the surface of separate intermediate member P. Then each member P was treated at 150℃ to obtain a specimen Q.

A BLB lamp light (0.5mW/cm^2) was irradiated against the specimen Q for a specified period to obtain a specimen. The water absorption rate of the specimen was less than 1%.

For the specimen and the intermediate member Q, the relation between the lamp irradiation time and the degree of hydrophilicity, the abrasion resistance, and the surface

hardness were determined.

[0025]

Fig. 2 shows the relation between the lamp irradiation time and the degree of hydrophilicity under a condition of changed ratio of solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin. The degree of hydrophilicity was evaluated by the contact angle with water.

The intermediate member Q did not show any change in contact angle with water. For all the specimens with the rate of additional 20 wt.%, 50 wt.%, 90 wt.%, and 95 wt.%, however, the contact angle with water decreased to about 3 deg. after 200 hr of irradiation. Also for the specimen with 5 wt.% content, the contact angle with water decreased to about 10 deg. within 200 hr of irradiation. It was proved that the specimens have favorable hydrophilicity.

[0026]

Fig. 3 shows the evaluation result on abrasion resistance. A rubbing abrasion was given to the surface of each specimen using a plastics eraser, then the change of appearance was observed. The criterion of the evaluation on the anti-abrasion characteristic is given below.

◎: No change occurred after 40 cycles of traverse.

○: Flaw appeared and the surface layer was separated after traversing cycles of 10 or more and less than 40.

△: Flaw appeared and the surface layer was separated after traversing cycles of 5 or more and less than 10.

×: Flaw appeared and the surface layer was separated after less than 5 cycles of traverse.

The result was that, at or less than 95 wt.% of the

ratio of the solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin, the evaluation was (○), and that the ratio is at or less than 90 wt.%, the evaluation was (◎).

[0027]

Fig. 4 shows the result of surface hardness determination. The evaluation of surface hardness was given by the hardness of pencil to generate flaw under scratch of pencils ranging from 6B to 9H in their core hardness. The hardness was about 5B for 90 wt.% of the ratio of the solid titanium oxide in the surface layer to the weight sum of the solid titanium oxide and the siloxane resin, and the hardness increased to H for 60 wt.% of the ratio to give a significant high hardness.

[0028]

[Effect of the Invention]

An outdoor member prevents the generation of black vertical stripe contamination on external wall surface of structures and buildings for a long time by forming a surface layer made of a photocatalyst and a hydrophilic material onto the substrate.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 illustrates an outdoor test device used in an example of the present invention.

[Fig. 2]

Fig. 2 shows the relation between the irradiation time of lamp light and the degree of hydrophilicization in an example of the present invention.

[Fig. 3]

Fig. 3 shows the relation between the amount of titanium oxide in the surface layer and the abrasion resistance in an example of the present invention.

[Fig. 4]

Fig. 4 shows the relation between the amount of titanium oxide in the surface layer and the surface hardness in an example of the present invention.

Outdoor exposed contamination test device

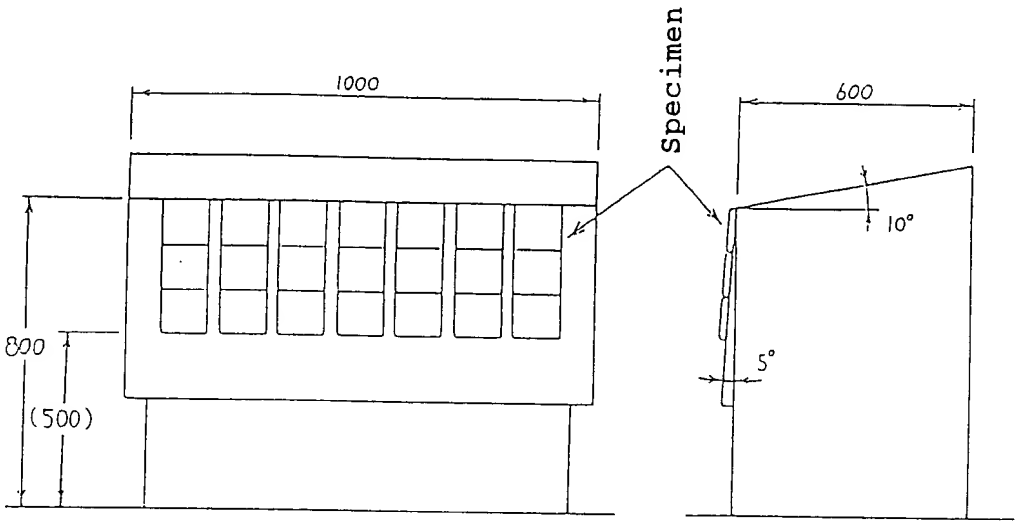

Fig. 1

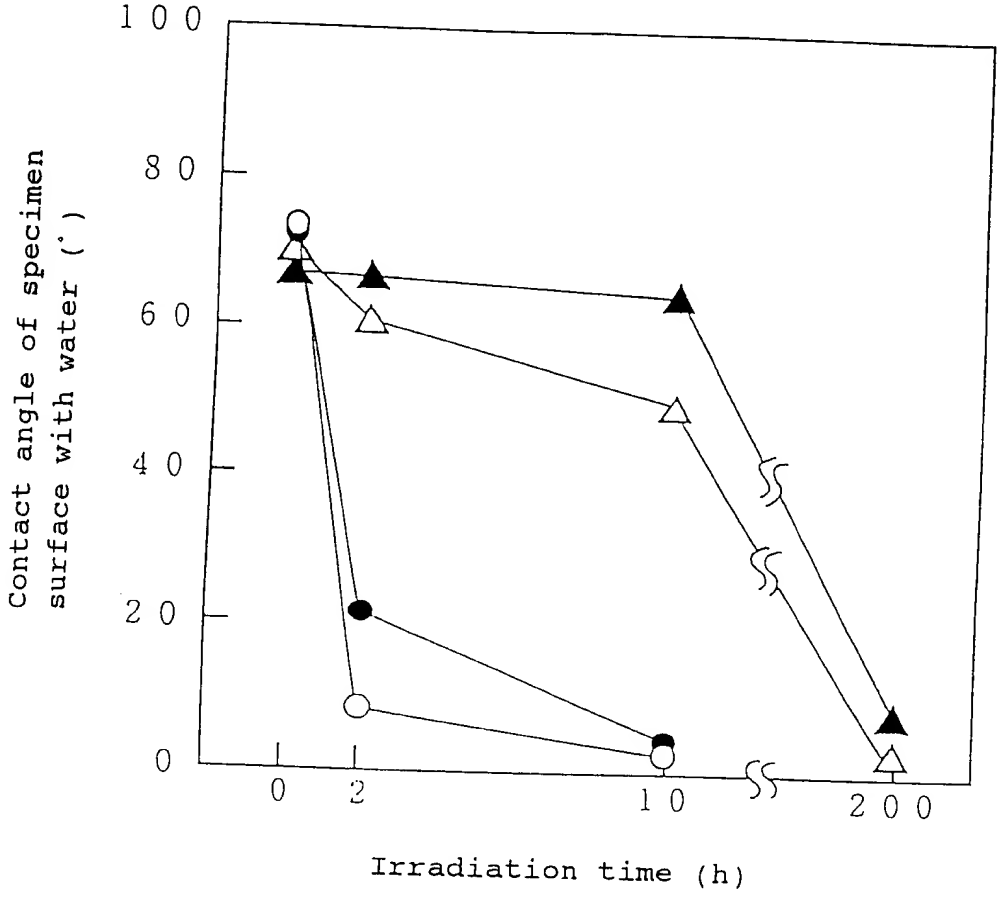
100
80
60
40
20
0
Contact angle of specimen surface with water (°)
0
2
10
200
Irradiation time (h)
▲ TiO2 5%
△ TiO2 10%
● TiO2 50%
○ TiO2 80%

Fig. 2

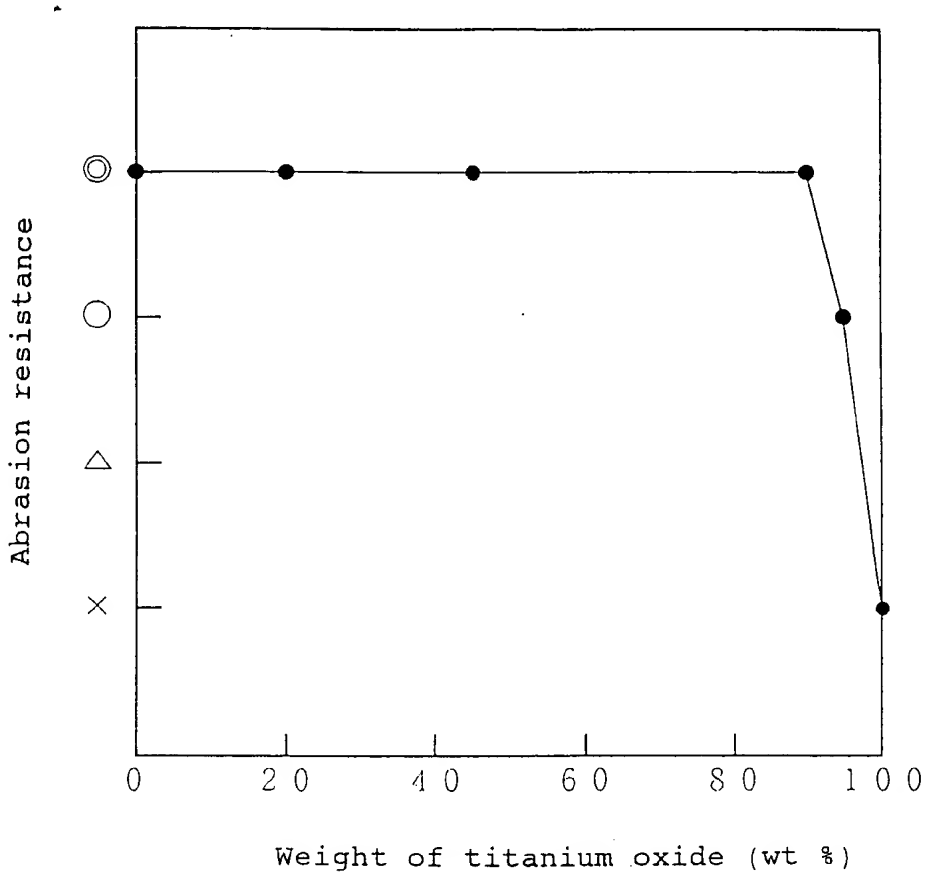
Abrasion resistance
◎
○
△
×
0
20
40
60
80
100
Weight of titanium oxide (wt %)

Fig. 3

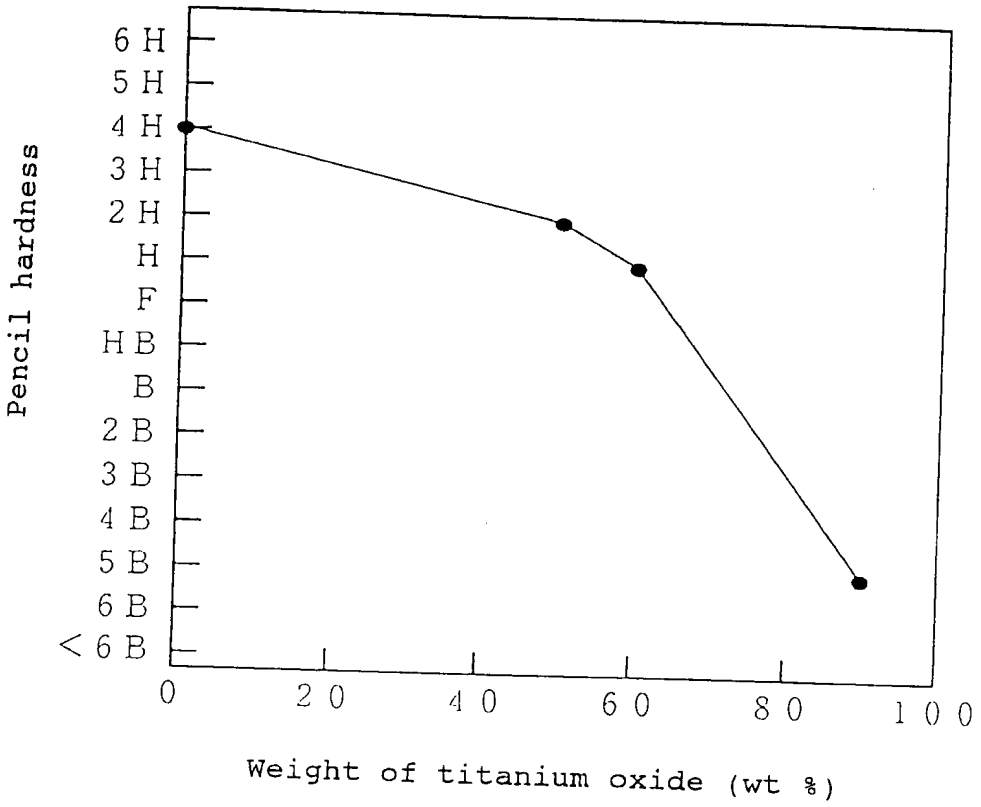
Pencil hardness
6 H
5 H
4 H
3 H
2 H
H
F
H B
B
2 B
3 B
4 B
5 B
6 B
< 6 B
0
2 0
4 0
6 0
8 0
1 0 0
Weight of titanium oxide (wt %)

Fig. 4

Abstract

[Object]

To provide an outdoor member to prevent generation of black vertical stripe contamination on external walls of structures and buildings for a long period.

[Conformation]

An outdoor member comprises a substrate, and a surface layer made of a photocatalyst and a hydrophilic material thereon.

[Selected Drawing]

None